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Short Communication

Graphene Modified $Li_3V_2(PO_4)_3$/C Composites with Improved Electrochemical Performances as Cathode Materials for Li-Ion Batteries

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Graphene modified $Li_3V_2(PO_4)_3$/C composites (Gr-LVPCs) are successfully synthesized through the rheological phase reaction method. The composite cathode material could deliver a high reversible capacity of 184.02 mAh g^{-1} with discharge capacity of 141.42 mAh g^{-1} after 100 charge/discharge cycles in the voltage range of 3.0-4.8 V at the current rate of 15 mA g^{-1}. Moreover, a high reversible capacity of 165.40 mAh g^{-1} with stable cycling can also be obtained at a current density of 90 mA g^{-1}. Those results suggest that graphene modification can be a powerful approach to improve the electrochemical performance of electrode materials, and Gr-LVPCs can serve as a very promising cathode material for rechargeable lithium batteries.

Keywords: $Li_3V_2(PO_4)_3$/C composites, graphene, rheological phase synthesis, lithium ion batteries, electrochemical performances

1. INTRODUCTION

Rechargeable lithium-ion batteries (LIBs) have attracted continuous attention for satisfying the commercial growing market of advanced portable electronics. Especially in recent years, LIBs are considered as the most promising power sources for hybrid electric vehicles (HEV) and electric vehicles (EV) [1-5]. However, the energy and power densities of current LIBs cannot meet the requirments of future devices. Therefore, high capacity, low-cost and environmentally-friendly cathode materials for LIBs are still actively explored [6,7]. Among the vast number of reported cathode materials [8-10], $Li_3V_2(PO_4)_3$ (LVP) has drawn particular interest because of its relatively high operate voltage, stable framework and large theoretic capacity [11-14]. Unfortunately, LVP suffers from its poor intrinsic electronic conductivity (2.4×10^{-7} S cm^{-1} at room temperature), which limits its application in high power batteries [15]. To solve this problem, several strategies have been developed, including electronically conductive materials coating [11,16-18] and metal ions doping [19,20].

Graphene (Gr) has recently been demonstrated as a great potential functional material because of its distinctive band structure and physical properties, such as high mechanical strength, superior thermal conductivity, and high electrochemical properties [21-24], so Gr is often used as an additive for electrode materials in LIBs [25-28]. In our previous work [11], $Li_3V_2(PO_4)_3/C$ composites (LVPCs) were successfully synthesized through the rheological phase reaction (RPR) method, and displayed good electrochemical performances. In the present work, we adopt Gr slurry (the moisture content is 92.8 wt.%) as an additive, and then Gr-LVPCs are in-situ chemically synthesized with the presence of Gr slurry. The Gr modified LVPCs may facilitate the electron migration and Li^+ diffusion throughout the LVP bulk particles, and thus enhance its electrochemical performance as the cathode for LIBs.

2. EXPERIMENTAL

Gr-modified LVPCs composites were prepared by rheological phase reaction (RPR) method similarly as those reported in previous literatures [29-31]. Firstly, the stoichiometric ratios of $LiOH\cdot H_2O$, V_2O_5, $NH_4H_2PO_4$, $C_6H_8O_7\cdot H_2O$ (citric acid monohydrate) (3.1:1:3:2) and different proportions of Gr slurry were mixed in stoichiometric amounts thoroughly by grinding. Later, the solid-liquid rheological body (muddy state) was obtained by adding a proper amount of redistilled water, then the rheological body was transferred into a cylindrical Teflon-lined stainless autoclave, and was humidified at 80 ^oC in a blast oven for 6 h. The as prepared mixture was dried at 100 ^oC for 10 h to obtain Gr-LVPCs precursor. Subsequently, the precursor was pre-heated at 350 ^oC for 3 h under nitrogen atmosphere in a tube furnace, followed by a slow cool to room temperature. Finally, the pre-heated material was ground and calcinated at 800 ^oC for 8 h under nitrogen flow to yield the Gr-LVPCs (referred to as 0.1 wt.%-Gr-LVPC, 0.3 wt.%-Gr-LVPC, 0.5 wt.%-Gr-LVPC, 1.0 wt.%-Gr-LVPC, and 2.0 wt.%-Gr-LVPC, respectively).

The structure and surface morphology of the LVPCs and Gr-LVPCs composites were characterized by X-ray diffraction (XRD) using Cu-Kα radiation, scanning electron microscopy (SEM, JSM-6510LV, JEOL), and transmission electron microscope (TEM, Philips Tecnai F20).

The charge-discharge measurements were carried out using 2016 type coin cells. The cells were assembled in an argon-filled glove box (JMS-3, Nanjing Jiumen Automation technology Co., Ltd), using a Li metal disc as the negative electrode and a commercial polyethylene (PE) film (ND420 H129-100, Asahi Kasei Chemical Co.) saturated with 1M $LiPF_6$ in Ethylene Carbonate (EC) and Dimethyl Carbonate (DMC) (1:1 v/v) (provided by Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd) as the electrolyte. The electrode film of Gr-LVPCs was consisted of 80% Gr-LVPCs, 10% super carbon, 10% polytetrafluoethylene microemulsion binder (PTFE, Xinxiang Yilida Batteries Materials Co., Ltd, 60 wt.%) and prepared by roll-pressing the mixture into a thick film and then pressing the film onto an aluminum net. The charge-discharge cycles were carried out at different current densities over a voltage range of 3.0-4.8 V on a multi-channel CT-3008W-5V5mA-S4 battery tester (Shenzhen Neware Electronics Co., Ltd).

3. RESULTS AND DISCUSSION

XRD patterns of LVPCs and Gr-LVPCs composites are shown in Fig. 1. The diffraction peaks of crystalline LVPC particles are clearly distinguishable, indicating well-ordered LVP structure. After modified by Gr, the crystalline structure of LVPC remained unchanged and no impurities were observed in all the Gr-LVPCs samples. However, both carbon and Gr were not detected by XRD, implying carbon is amorphous and the Gr content is very low [32,33].

The SEM (a-e) and TEM (f) images of as-synthesized Gr- LVPCs powders are presented in Fig. 2. From the SEM images in Fig. 2a-e, we can find that the particle size of the Gr- LVPCs became smaller and smaller with the increase in Gr content, which indicates that Gr modification can suppress the crystal growth of LVPCs [34]. From the TEM image of Fig. 2f, it is observed that the LVPCs particles are wrapped loosely by Gr multilayer films, which can construct a 3D conductive framework to greatly enhance the electronic/ionic conductivity of the composites and minimizes the vanadium dissolution [35,36].

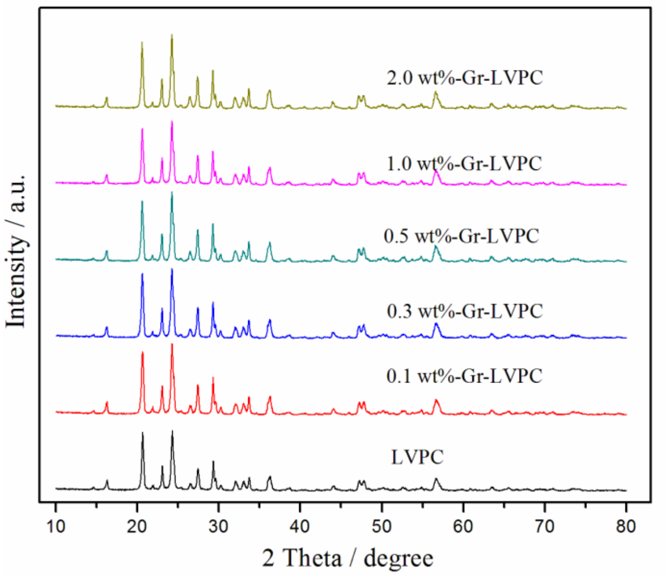

Figure 1. XRD patterns of LVPC and Gr-LVPCs composites.

Fig. 3a shows the initial charge and discharge profiles of as-synthesized LVPC and Gr-LVPCs in the potential range of 3.0-4.8 V at the current density of 15 mA g^{-1}. The voltage profiles of the six composite cathodes all exhibit three discharge voltage plateaus, which are attributed to the transition processes of LVP during the electrochemical reactions, in agreement with the previous reports [37,38]. The 0.1 wt.%-Gr-LVPC , 0.3 wt.%-Gr-LVPC, 0.5 wt.%-Gr-LVPC, 1.0 wt.%-Gr-LVPC, 2.0 wt.%-Gr-LVPC and LVPC cathodes deliver initial discharge capacity of 161.49, 174.24, 184.02, 168.63, 166.2, and 160.39 mAh g^{-1}, respectively. Compared to the LVPC, the Gr-LVPCs electrodes have longer charge/discharge curves and higher initial discharge capacity, which is because that the electronic conductivity of LVPC is poorer than Gr-LVPCs. The effect of Gr modification is even more significant when compared the cycling performances of all the cathodes. As shown in Fig. 3b, the cycling stability of the Gr-LVPCs composites are better than the LVPCs. Particularly, the 0.5 wt.%-Gr-LVPCs sample has the highest initial discharge capacity and retains a capacity of 141.42 mAh g^{-1} after 100 cycles, demonstrating an excellent cycling stability and a high lithium storage capability which relies on the specific structure of the sample.

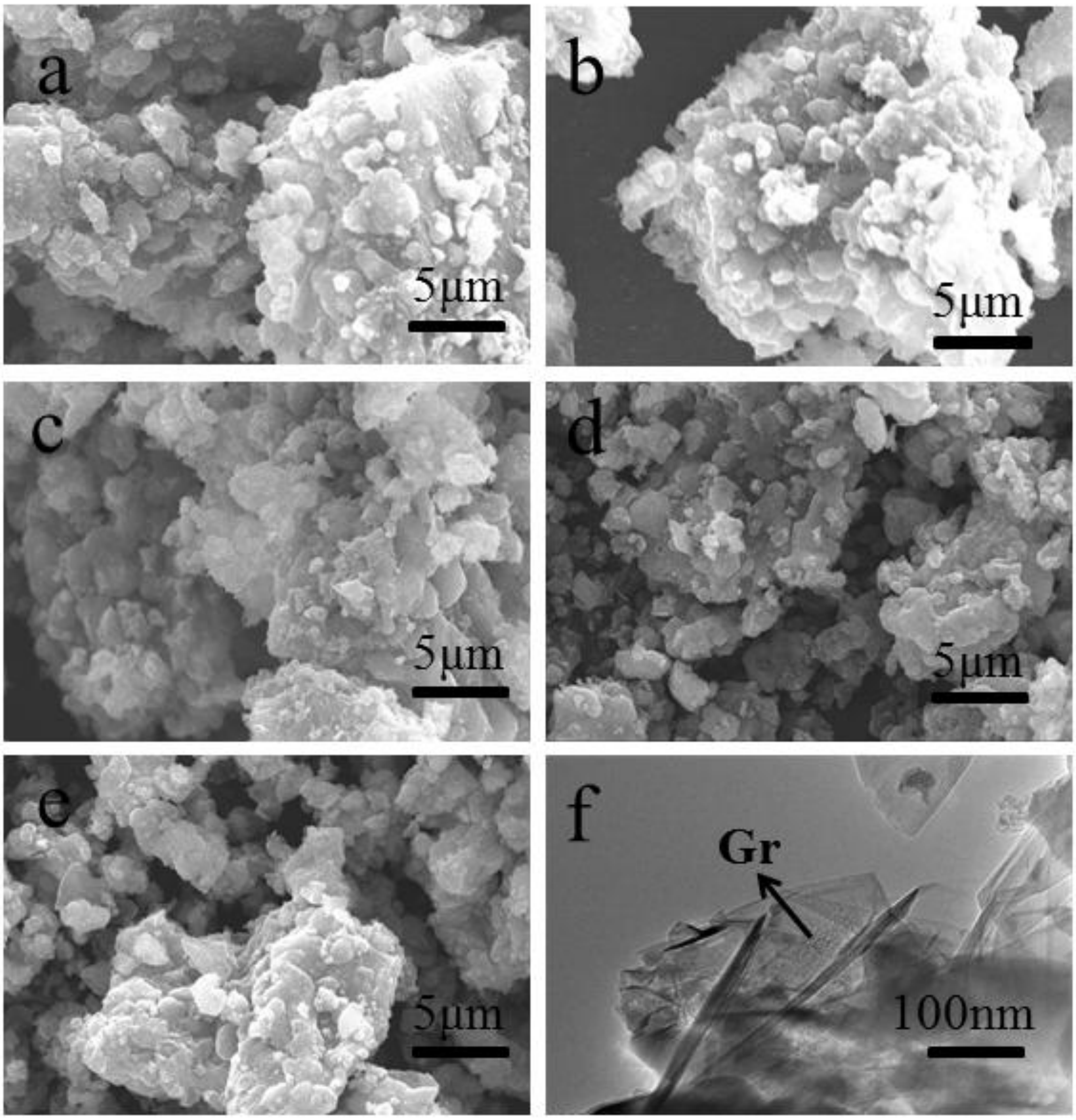

Figure 2. SEM images of Gr-LVPCs (a) 0.1 wt.%-Gr-LVPC, (b) 0.3 wt.%-Gr-LVPC, (c) 0.5 wt.%-Gr-LVPC, (d) 1.0 wt.%-Gr-LVPC, (e) 2.0 wt.%-Gr-LVPC, and (f) TEM image of 0.5 wt.%-Gr-LVPC.

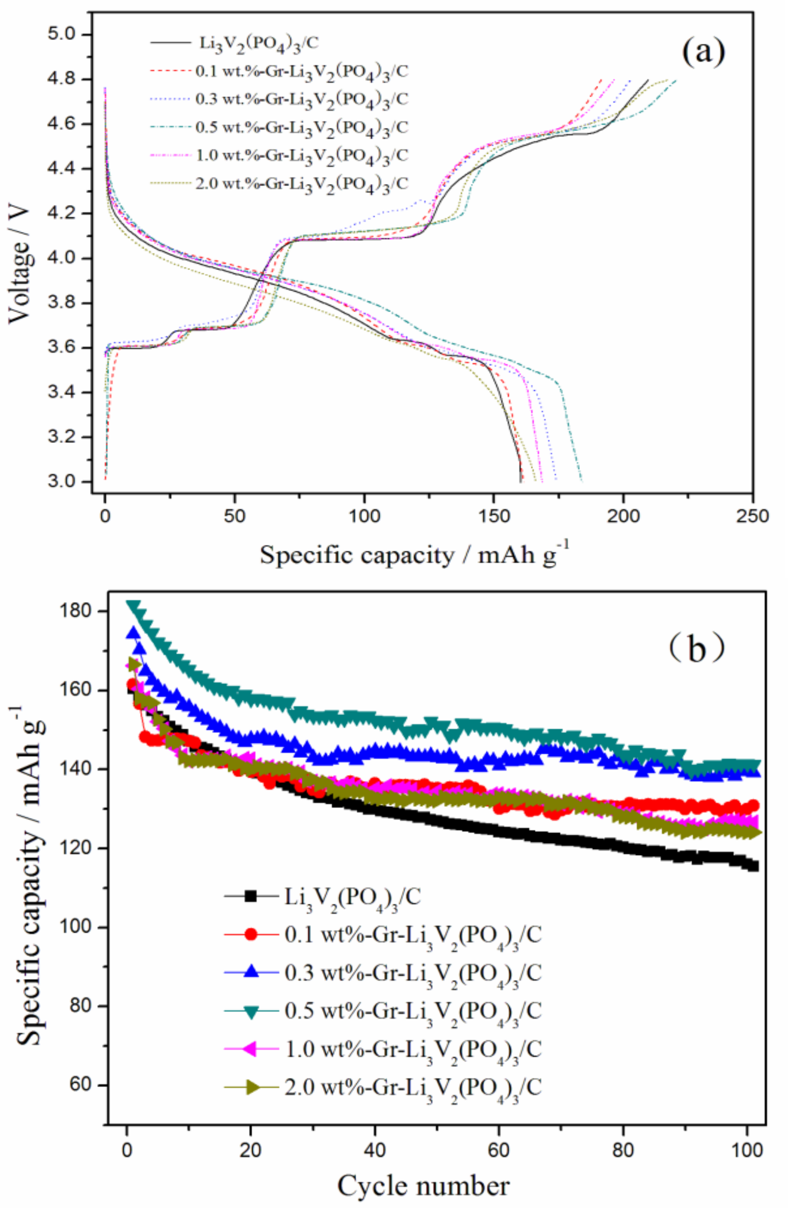

Figure 3. Electrochemical performance of LVPC and Gr-LVPCs in the potential range of 3.0- 4.8 V at the current density of 15 mA g^{-1}: (a) initial charge/discharge curves, (b) cycling performance.

The cycling performance of the 0.5 wt.%-Gr-LVPC and LVPC electrode at different current densities is given in Fig. 4. It is obvious that Gr-LVPCs have much better electrochemical performance than that of pure LVPCs. As shown in Fig. 4a, The 0.5 wt.%-Gr-LVPCs electrode delivered the initial reversible capacities of 184.02, 181.63, 169.70, 169.32, and 165.40 mAh g^{-1} at the current densities of 15, 30, 45, 60, and 90 mA g^{-1} and retained 78%, 77.8%, 81.7%, 78.5% and 79.6% of the initial capacity up to 100 cycles, respectively. However, the reversible capacity of LVPC is 122.36 mAh g^{-1} after 100 cycles at a rate of 15 mA g^{-1}. Upon increasing the rate to 90 mA g^{-1}, its reversible capacity is maintained at 111.87 mAh g^{-1}. These data demonstrate that the Gr-LVPCs have higher rate capability and structural stability. All of this performance attributed to the homogenous distribution of highly conductive Gr around LVPCs particles, which serve as a fast path for electron migration during the charge-discharge processes.

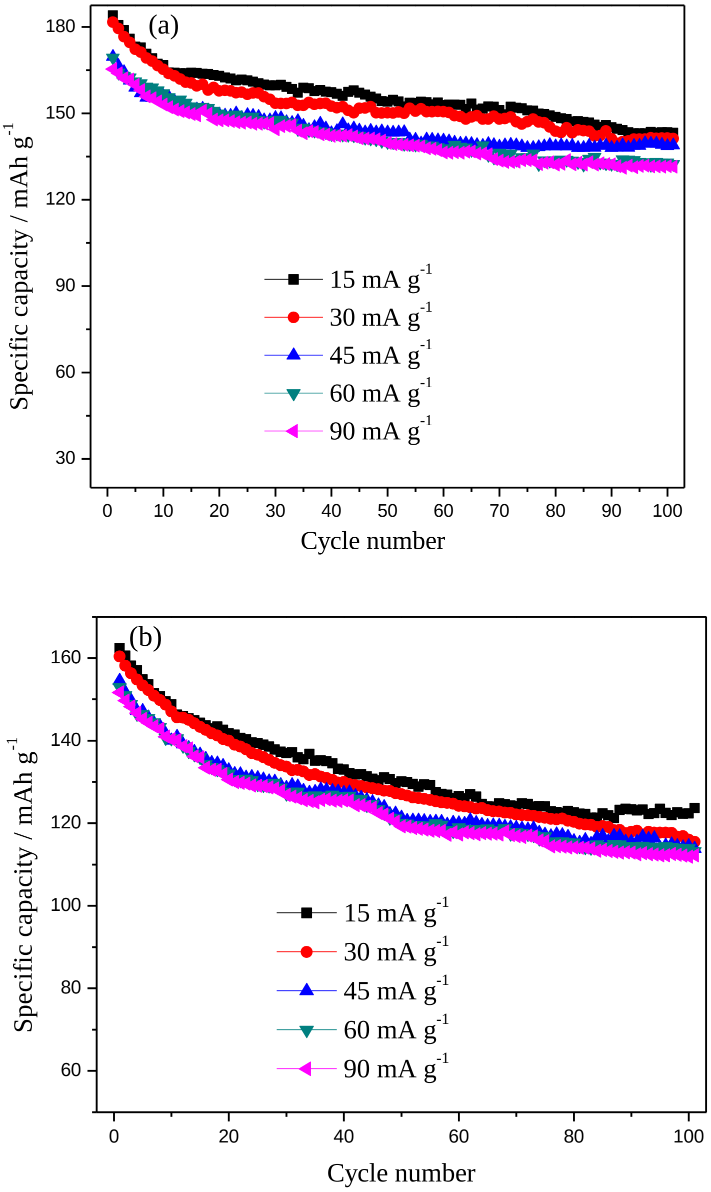

Figure 4. The cycling performance of 0.5 wt.%-Gr-LVPC (a), and LVPC (b) electrode at different current densities in the potential range of 3.0-4.8 V.

4. CONCLUSIONS

In summary, Gr-LVPCs composites with different graphene content have been successfully synthesized by RPR method. The 0.5 wt.%-Gr-LVPC composite shows the best electrochemical performance which exhibits an initial discharge capacity of 184.02 mAh g^{-1} with capacity retention of 78% after 100 cycles in the voltage range of 3.0-4.8 V. Even at a high current density of 90 mA g^{-1}, the electrode can still deliver a high capacity of 165.40 mAh g^{-1} with small capacity decay upon cycling.

The superior electrochemical performance, combined with the facile synthesis strategy suggests the use of these Gr-LVPCs as promising cathode materials for rechargeable lithium batteries.

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